

2.6 COUPP Vapour Exposure Hazard Analysis

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Executive Summary

The COUPP experiment at SNOLAB uses two potentially hazardous volatile substances. propylene glycol and iodotrifluoromethane (CF_3I). This note describes the pertinent exposure limits to these chemicals as set by legislation, the American Conference of Governmental Industrial Hygienists (ACGIH), and the American Industrial Hygienists Association (AIHA).

The exposure limits cited by these organizations are generally Time Weighted Averages (TWAs) averaged over an 8 hour shift. A Short-Term Exposure Limit (STEL) of 3 times TWA should not be exceeded for more than 30 minutes and a Ceiling limit (C) of 5 times the exposure limit should never be exceeded.

For propylene glycol, AIHA sets a Workplace Environment Exposure Limit (WEEL) TWA of $10\text{mg}/\text{m}^3$ of aerosols or vapour. This limit is much smaller than legislated limits. The C would be reached by an evaporating area of 300cm^2 and the STEL would be reached by an evaporating area of 180cm^2 . The latter limit corresponds to a 15cm (6") diameter circle. Cleanup workers exposed to more than the C or handling workers exposed to more than the STEL will require at least half-mask respirators with organic vapour (OV) filters. If there will be more than 2.5 hours of exposure to glycol, the TWA should be calculated.

For CF_3I , ACGIH sets a Threshold Limit Value (TVA) of 150ppm TWA. Should the full 4-kg of CF_3I be released into the drift, once mixed with the drift air it would be at 1.4 times the TWA concentration. The fresh air makeup into the drift would bring the concentration below the TWA within 15 minutes. The Ceiling limit may be exceeded downwind of the experiment before the gas mixes.

CF_3I handling will be done with a closed system. The transfer line will need to be leak checked to ensure the system is closed. The only CF_3I workers will be exposed to is during venting of the transfer line prior to disassembly. Given a 39mL volume of pressurized CF_3I gas, a 45cm (18") sphere would be filled just beyond the STEL. As long as the line is vented away from workers, no additional PPE will be required for CF_3I transferring operations.

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Limits, Regulations, and Definitions

The Ontario Occupational Health and Safety Act of 1990, [Regulation 833, Control of Exposure to Biological or Chemical Agents](#), sets limits on the exposure to hazardous chemicals in the workplace. Quoting Paragraph 4,

Without limiting the generality of section 3, every employer shall take the measures required by that section to limit the exposure of workers to a hazardous biological or chemical agent in accordance with the following rules:

1. If the agent is listed in the Ontario Table, exposure shall not exceed the TWA, STEL, or C set out in the Ontario Table.
2. If the agent is not listed in the Ontario Table but is listed in the ACGIH Table, exposure shall not exceed the TWA, STEL, or C set out in the ACGIH Table.
3. If the Table that applies under paragraph 1 or 2 sets out a TWA for an agent but sets out neither a STEL nor a C for that agent, *exposure shall not exceed the following excursion limits:*
 - i. Three times the TWA for any period of 30 minutes.
 - ii. Five times the TWA at any time.
4. Paragraph 3 does not apply with respect to an agent that is prescribed as a designated substance under Ontario Regulation 490/09 (Designated Substances) made under the Act. O. Reg. 491/09, s. 4.

The 3 and 5 times multiplication factors are taken directly from [ACGIH](#).

Excursion Limits. For many substances with a TLV–TWA, there is no TLV–STEL. Nevertheless, excursions above the TLV–TWA should be controlled, even where the 8-hour TLV–TWA is within recommended limits. Excursion limits apply to those TLV–TWAs that do not have TLV–STELs.

Excursions in worker exposure levels may exceed 3 times the TLV–TWA for no more than a total of 30 minutes during a workday, and under no circumstances should they exceed 5 times the TLV–TWA, provided that the TLV–TWA is not exceeded.

ACGIH also carefully defines the units used in its [Introduction to BEIs and TLVs](#) .

TLV Units TLVs for gases and vapors are established in terms of parts of vapor or gas per million parts of contaminated air *by volume* (ppm), but may also be expressed in mg/m^3 . [...] Where 24.45 = molar volume of air in liters at NTP conditions (25 C and 760 torr), the conversion equations for gases and vapors [$\text{ppm} \leftrightarrow \text{mg}/\text{m}^3$] are as follows:

$$\text{TLV in ppm} = (\text{TLV in mg}/\text{m}^3) (24.45)$$

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$$\text{OR}$$

$$\text{TLV in mg/m}^3 = \frac{(\text{TLV in ppm}) (\text{gram molecular weight of substance})}{24.45}$$

Propylene Glycol**Limits**

Propylene Glycol is listed under Paragraph 9, the Ontario Table, of Regulation 833 with

1. a TWA of 50ppm or 155mg/m³ of vapour or aerosol,
2. or a TWA of 10mg/m³ of aerosol for assessing the visibility in a work environment where 1,2-propylene glycol aerosol is present.

As no aerosol is being formed the first limit is legally applicable.

The Mallinckrodt Baker, Inc. [MSDS](#) P6928 for propylene glycol lists the AIHA Workplace Environmental Exposure Limit (WEEL) of 10mg/m³ TWA. This limit is also posted in the [2010 WEEL Values](#) from AIHA. ACGIH does not have a TLV for propylene glycol. The lesser of the AIHA limits for propylene glycol exposure will be used by COUPP.

Hazard Assessment

Glycol handling activities include being near open glycol containers or glycol spills, and the opening of glycol containers. Glycol filling is a reasonably lengthy process for which the TWA should not be exceeded. Small spill glycol cleanup and the opening of glycol containers are quick procedures that are performed less than 30 minutes per day, therefore Ceiling Limit would apply to them.

To determine the concentration of glycol vapours near an open container of glycol, Gauss' Law will be used to match the flux of glycol vapour crossing a hemisphere at the open bucket to the flux exiting the drift. The flux of air mixing at the edge of the drift is known, and is assumed to be proportional to the size of the Gaussian surface. The concentration of glycol is the proportion of these two fluxes. Therefore, the concentration of glycol decreases as 1/r² as one moves away from the open container.

From the [MSDS](#), at 25°C, the vapour pressure of propylene glycol is 0.129mmHg and it has a molecular mass of 76.09 g/mol. The partial pressure converts to 1.70×10⁻⁴ atm, 170ppm, 529mg/m³, or 53 times the Ceiling Limit. This is the maximum possible concentration of glycol vapours. Assigning this concentration to the edge of the open container, the concentration at r is given by

$$\rho_{\text{glycol}} = 529 \text{ mg/m}^3 \frac{A_{\text{surf}}}{\pi r^2}$$

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From a 700cm² bucket opening, the TWA limit would be reached at a distance of 1.2m, the STEL at 69cm, and the Ceiling Limit would be reached at 53cm. At a working distance of 45cm, the glycol concentration would be 5.8 times the TWA. At least a half face respirator would be required to work with glycol out of an open bucket. A barrier or a guard would be required 1.5m from the open glycol to mark the hazard.

If one has to breath closer than 45cm from glycol contamination, such as when cleaning residue from buckets, a full face respirators should be worn. These respirators provide adequate protection against glycol vapours up to a TWA concentration of 500mg/m³, or just below the vapour pressure of glycol. Such a condition exists when cleaning glycol residue from containers.

Glycol may be worked out of smaller containers without respirators and without exceeding the TWA or STEL. The STEL would be reached by a 360cm² container opening. Given that such a container would have a contaminated lid associated with it, no container with an opening greater than 180cm² or a diameter greater than 15cm (6"), should be opened without a respirator, and such a large container should not be handled for more than 2.5 hours/shift. Smaller containers may be handled for longer in inverse proportion to the area of their opening.

For spill cleanup, the ceiling limit would be reached when working 45cm away from a 600cm² puddle of glycol. Given that cleanup generally increases the surface area of a spill, no spill with a surface area greater than 300cm² should be cleaned up without a respirator. This area is approximately the size of an unfolded paper towel or a sheet of paper absorber.

CF₃I

Hazards and Limits

Trifluoroiodomethane, CF₃I, is not listed in Regulation 833, but it's TWA is listed in ACGIH as 150ppm (1.20g/m³). By Regulation 833 and by best practices, the ACGIH TWA is to be used, and the Short-Term and Ceiling Exposure Limit can be calculated from it by multiplying by 3 and 5 respectively. The STEL is 450ppm (3.61g/m³), and the Ceiling Limit is 750ppm (6.01 g/m³). Above a concentration of 0.2%, CF₃I has been shown to affect sensitivity to adrenaline and cardiac function in canines.

CF₃I is both colourless, odorless and has a boiling point of -22.5 °C. Gas escaping from an open container of CF₃I will be significantly colder than the surrounding air, and will fall to the floor in the absence of turbulent mixing. A large release of CF₃I will be hazardous for those unaware of its release, and who breath air near the ground. In thermal equilibrium, after mixing with air or passing through an AHU, CF₃I will distribute evenly in height.

There are three situations in which CF₃I may be released. When purging transfer lines, a small planned release of CF₃I will occur. Accidental releases of CF₃I may be a slow leak

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of the gas during handling, or a rapid catastrophic failure of both the pressure vessel and inner vessel.

Planned Releases

CF₃I will need to be purged from a 18" long 1/4" transfer line with 0.065" wall thickness at up to 80psi at the end of CF₃I filling or draining operations. The transfer line will contain up to 39mL at 80psi and 25°C, or 1.7g of CF₃I. I assume that a person releasing the line pressure stands 45cm with the stream of escaping gas pointed away. A 45cm sphere has a volume of 0.382m³. This can be filled with 2.3g before exceeding the Ceiling Limit. This limit would not be exceeded during a transfer line purge, and the period of exposure is minimal. No additional PPE is required to purge the transfer line.

Accidental Releases during CF₃I handling

An accidental release of CF₃I during transfer operations would involve leaks, the accidental opening of an exterior valve, or the failure of a connector. 40mL of CF₃I at STP would have to leak before the TWA in a 40cm sphere would be exceeded. This size of leak can be easily prevented by vacuum checking the transfer line prior to pressurization and the use of Snoop leak checker when pressurized with CF₃I. An Ashcroft pressure calibration gauge will be connected to the transfer line during the vacuum leak check and filling. It would easily detect a 40mL/6min CF₃I leak rate, equivalent to a 3.3%/min (25 torr/min) loss of vacuum. After a passed vacuum check and the pressurization of CF₃I lines, Snoop leak checking can be performed to verify that there are no leaks around valves, or around other joints that did not leak under vacuum. Sensitive handheld CF₃I leak checkers are on order by COUPP that would be more sensitive than a Snoop check.

J Drift Ventilation

Ventilation in J Drift is provided by AHU-14. Air from AHU-14 ventilates K and N Drifts, part of F Drift, and Stage #1 of J Drift. AHU-14 circulates 13,710 cfm (390 m³/min) of air to this area, of which at least 2,020cfm (57.5 m³/min or 3450m³/hr) is fresh air. This is able to recirculate the full volume of air once every 6 minutes, and it results in a 30 minute half-life for contaminants in the drift's air.

Drift	J	K	F	N	Total
Volume in m ³	850	350	950	350	2400

Table 1: Volume of drifts ventilated by AHU-14.

Accidental Releases of Full Volume

A full accidental release of 4kg of CF₃I would produce 510L of gas, and is capable of contaminating 670m³ of air at the Ceiling Limit, or 3340m³ to the TWA limit. Should the entire volume handled by AHU-14 be evenly mixed with this amount of CF₃I, the concentration of CF₃I would decay as

$$\rho = \rho_o \exp(-t/42\text{min})$$

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and a worker's TWA for a shift in this environment would be

$$\rho_{TWA} = 1.7 \text{ g/m}^3 \frac{42 \text{ min}}{8 \text{ hr}} (1 - \exp(-8 \text{ hr}/42 \text{ min})) = 0.15 \text{ g/m}^3$$

which is 12% of the TWA limit. No limits are exceeded in the drift if 4-kg of CF₃I are evenly mixed.

On its way to AHU-14, the local concentration of CF₃I may be above the Ceiling Limit. At the junction of J drift and F drift, near AHU-14, the forced airflow of 320m³/min would produce a wind of 17 cm/s. Assuming that CF₃I disperses into a cross-section 2m wide by 1m high, the full mass of CF₃I would have to disperse more quickly than 5.5min, or 1.5L/sec, in order to exceed the Ceiling Limit directly down stream of the experiment. While the bubble chamber is outside of its water shielding, such a discharge, and the shattering of the inner vessel, should be sufficiently noticeable to alert personnel near the experiment of the hazard, and to let them evacuate to good air.

When the chamber is surrounded by water shielding, the visual and auditory clues of a large release will be hidden and muffled. The water shielding does provide an 2m³ intermediate air volume that will temper the loss of CF₃I. In a rapid release, this intermediate volume would have 0.5m³ of CF₃I dumped into it. The CF₃I would be dumped high in the volume, displacing and forcing clean air out the bottom. A slow release on the order of >2 minutes would allow the CF₃I to thoroughly mix and escape the intermediate volume. However, such a release would be diluted by four, and sufficiently slow to avoid exceeding the Ceiling Limit. Thus, either the speed of the release or the CF₃I mixing with air before release saves SNOLAB personnel from the hazards of a CF₃I release.

The noise of the glass vessel shattering, of the pressure relief popping, or of the glycol or water boiling would provide would indicate a CF₃I leak. If a CF₃I release is noticeable, personnel should evacuate F drift between the experiment and the air handlers and wait 15 minutes before reentering. Otherwise, there is no need to evacuate from a CF₃I release.